

**METHOD OF PROCESSING SULFUR-CONTAINING MATERIALS DERIVED FROM  
FLUE GAS DESULFURIZATION OR OTHER SOURCES**

**BACKGROUND OF THE INVENTION**

**FIELD OF THE INVENTION**

5           The present invention relates to the field of processing sulfur-containing materials such as poorly soluble metal sulfides derived from flue gas desulfurization or other sources.

**DESCRIPTION OF THE BACKGROUND ART**

10           In recent years governmental and other bodies have become increasingly active in resisting air pollution. Concentration of SO<sub>2</sub> in the atmosphere is one form of air pollution that has been particularly objectionable. In the past, industrial facilities  
15           such as electrical power plants and other steam generating facilities, sulfuric acid plants, metal smelters and petroleum refineries merely vented their flue gases containing sulfurous emissions to the atmosphere. The growth and concentration of industrial facilities emitting sulfur oxides gradually increased  
20           the ground level SO<sub>2</sub> concentrations and airborne particulate sulfates derived from SO<sub>2</sub> to levels considered to constitute harmful pollution.

25           Initially, the problem of reducing ground level SO<sub>2</sub> concentrations was solved by high stacks which would more widely distribute the SO<sub>2</sub> to maintain the SO<sub>2</sub> concentration at ground level to less than the threshold polluting level. Further expansion of industry and an awareness of the mechanisms by which SO<sub>2</sub> is converted to harmful sulfate particulate dispersions in  
30           the atmosphere have caused tightening of governmental-imposed SO<sub>2</sub>

pollution limits which has forced both industry and government to seek processes for reducing or eliminating SO<sub>2</sub> pollution.

5 A number of processes have been commercially installed for the purpose of reducing SO<sub>2</sub> emissions either by flue gas desulfurization (FGD) or by removing the sulfur from the fuel prior to combustion such as by gasification. These processes have been successful to varying degrees.

10 Sulfur dioxide is recovered in common commercial practice from waste gases, such as flue gas from the burning of coal or other sulfur bearing fuels, using absorptive processes such as wet scrubbing with lime or limestone slurries, lime or limestone dry injection, or lime or limestone slurry injection spray drying  
15 which is preferable for the purposes of this invention. Each of these processes produce a waste product comprised of calcium sulfate, calcium sulfite and calcium carbonate contaminated with impurities such as gangue, heavy metal salts, fly ash and unburned carbon introduced with the lime or limestone as well as  
20 from the fuel. Wet scrubbing has the advantages of higher utilization of the lime or limestone and lower residual sulfur dioxide content in the effluent waste gas but produces the waste product as an aqueous slurry which must be either disposed in a pond or dried before processing. Dry scrubbing by injection into  
25 the firebox or lime/limestone slurry injection spray drying have the advantages of higher stack gas temperature for better plume dispersal and less water in the plume hence less plume visibility and of producing the waste product as a dry powder usually in a bag-house installed to also remove particulate material such as  
30 fly ash. Dry injection scrubbing has a lower efficiency of lime/limestone utilization and a higher concentration of sulfur dioxide in the effluent stack gas. Lime or limestone slurry

injection spray drying combines the advantage of greater sulfur dioxide removal, as in the wet scrubber, with the advantages of less water vapor in the stack gas, less plume visibility, better dispersion due to higher stack gas temperature and a dry product.

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Processes for the cleanup of stack gases or fuel gasification can be classified either as "throwaway" or "recovery" types depending on the manner of disposition of the absorbed  $\text{SO}_2$ . The "throwaway" processes are characterized by the conversion of  $\text{SO}_2$  to, for example, calcium sulfite or calcium sulfate, or a mixture thereof combined with fly ash and residual calcium carbonate or lime, or by the conversion of sulfur in solid fuel as it is gasified or liquified to hydrogen sulfide gas which is then absorbed by calcium oxide to form calcium sulfide mixed with impurities from the original fuel, which is discarded such as in a landfill. Material containing calcium sulfate or calcium sulfite might in some instances be processed to manufacture useful gypsum products but it is more often discarded such as in a landfill from which it can be leached into ground water. Thus the "throwaway" processes help to improve air quality but generally require the use of valuable land for waste disposal, make no profit because they do not make useful products and may cause secondary water pollution because water soluble components in the waste may be leached by rain water and pollute ground waters due to the contained sulfite which has a high chemical oxygen demand. Metal sulfides contained in landfills also can be oxidized by air to form sulfuric acid run off in surface water. The "recovery" processes are regenerable in that they absorb the  $\text{SO}_2$  from the waste gas and then produce either elemental sulfur or industrially useful sulfur compounds such as sulfuric acid or liquefied sulfur dioxide while returning the absorbent material to its original condition for recycle and the

absorption of additional SO<sub>2</sub>. Such regenerable "recovery" processes in the past generally have been more expensive to build and more expensive to operate than the simpler calcium carbonate, oxide or hydroxide based "throwaway" processes even after taking credit for the value of the products manufactured.

U.S. Patent No. 4,083,944 to the present inventor, Franklin S. Chalmers is directed toward one prior art regenerative process for flue gas desulfurization.

U.S. Patent No. 5,607,577 to Koszarycz et al. is directed to equipment and process involving addition of calcium oxide to Athabaska tar sand native to Alberta, Canada, to prevent the emission of sulfur dioxide when the residual coke on the spent sand is combusted, thus primarily avoiding the need for and expense of separate flue gas desulfurization equipment. There is some redistribution of the end products to which the various forms of sulfur report. Those include solid compounds of calcium and sulfur, liquid hydrocarbon-sulfur compounds and hydrogen sulfide gas. The solid compounds of calcium and sulfur from this process, which is an alternative to flue gas desulfurization (FGD) processes are similar in composition to products of various flue gas desulfurization (FGD) processes. This process assumes those products are thrown away.

U.S. Patent No. 5,433,939 (the '939 patent) to Thomas D. Wheelock appears to be a continuation of development of the Iowa State University (ISU) process by Dr. T.D. Wheelock (U.S. Patent 4,102,989) which is intended primarily to convert calcium sulfate and calcium sulfite to calcium oxide with the evolution of sulfur dioxide. That earlier process under certain conditions has an undesired preferential production of calcium sulfide. It appears

that Dr. Wheelock has addressed that earlier deficiency of his process. The process described in the '939 patent starts with calcium sulfide fed to a fluid bed gas-solid high-temperature oxidation-reduction reactor either having two zones or a single zone operated in two cyclic alternating modes wherein calcium sulfide is alternately oxidized to calcium sulfate and reduced stepwise to calcium oxide, ultimately oxidizing all the calcium sulfide feed material to calcium oxide and sulfur dioxide. There are high operational costs and control problems inherent in the delicate balance of alternating oxidation and reduction in the ISU process, and problems and costs involved with manufacturing, storing and transporting sulfur dioxide or sulfuric acid as products. Column 1, lines 14-33 in this patent describe a need in the art for dealing with waste calcium sulfide.

U.S. Patent No. 5,653,955 to Thomas D. Wheelock is an improvement patent on the earlier cited Wheelock '939 patent. This patent extends the earlier described gas-solid high-temperature oxidation-reduction process from fluid bed reactors to also include fixed and moving bed reactors and goes into somewhat more detail as to the mechanisms of the earlier patented process.

U.S. Patent No. 5,037,450 to Keener et al. relates to apparatus and process to remove sulfur and nitrogen compounds from coal with the sulfur reporting to a sorbent material specified (column 5, lines 25-33) to be preferably calcium oxide or calcium carbonate. The spent sorbent is collected in the form of calcium sulfide for regeneration in an unspecified manner (column 4, lines 10-13). The patent states (column 5, line 68 to column 6, line 1) that the spent sorbent, CaS, can be subsequently regenerated to CaO in a separate operation, not

shown, and further states (column 6, lines 52-54) that since the spent sorbent (CaS) can be regenerated to CaO, the apparatus will reduce the output of solid waste.

5 U.S. Patent NO. 4,824,656 to Rice et al. speaks (column 1, lines 9-11) of dissolving a sulfur-containing catalyst in liquid ammonia solution and separating the ammonia therefrom in order to recover the elemental sulfur. But in column 2, lines 48-52 it is clear that the catalyst such as activated carbon saturated with  
10 elemental sulfur is to be extracted with anhydrous ammonia liquid to dissolve the sulfur leaving behind the insoluble carbon catalyst. Second, the prior art description (column 1, lines 25-52) talks of high temperature methods, with U.S. patent citations, for recovering sulfur dioxide with the concurrent  
15 production of lime and states (column 1, lines 42-45), "All of the above methods require very high temperature and none of them disclose the recovery of catalyst used in removal of the sulfur." Third, the process cited to produce the sulfur laden solid catalyst to which this patent is related is described (column 2,  
20 lines 32-40) as having already thermally reduced the gypsum to calcium sulfide, "The calcium sulfide is converted into ammonium sulfide and/or ammonium bisulfide, which in turn is oxidized to sulfur using a suitable catalyst." An aqueous slurry of CaS apparently is reacted with ammonia,  $\text{NH}_4\text{OH}$ , precipitating calcium  
25 hydroxide and an aqueous solution of ammonium sulfide and/or ammonium bisulfide is then (column 5, lines 22-26) contacted with activated carbon catalyst and air in a column to produce the sulfur laden carbon catalyst.

Calcium, Strontium and Barium

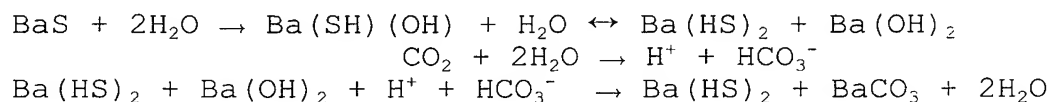
Calcium, strontium and barium, elements collectively known as the alkaline earths, are closely related in the chemical periodic table and have chemical properties generally similar to one another, but some specific chemical properties which are substantially different.

Prior Barium Sulfide Technology

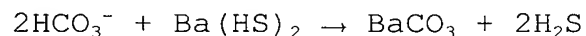
Technology has been known since the early to mid 19th century and commercially practiced for much of that time in the United States to produce barium compounds by the roasting with coal of barite ore, a form of barium sulfate, to produce black ash from which barium sulfide is leached with water. A barium sulfide solution of technical grade purity is the starting point for the production of many other barium chemicals. For example barium carbonate is made by the addition of soda ash or of carbon dioxide typically as contained in flue gas; barium chloride by the addition of calcium chloride or hydrochloric acid; barium sulfate or blanc fixe by the addition of salt cake; barium nitrate by the addition of Chilean salt petre, etc. The key to the preparation of technical grade solution is the water leaching of barium sulfide black ash in order to separate a commercially pure solution of barium sulfide from insoluble gangue and other impurities. Barium sulfide is very soluble in water and a recovery or yield of 95% more or less is commonly attained.

In the conventional commercial processing of a barium sulfide solution to produce the carbonate salt, carbon dioxide is introduced into a batch of aqueous sulfide liquor, often in the form of flue gas from the combustion of fuel such as coal or oil,

in order to precipitate commercially pure barium carbonate and ultimately to release hydrogen sulfide gas. Those practiced in the art are aware that during the initial carbonation period carbon dioxide is absorbed with no evolution of hydrogen sulfide because the barium sulfide solution hydrolyzes to form barium hydrosulfide and barium hydroxide from which the hydroxide selectively reacts with bicarbonate ions to precipitate barium carbonate.



Barium hydrosulfide precipitates as barium carbonate with the continuing addition of carbon dioxide only after all the barium hydroxide has been consumed.



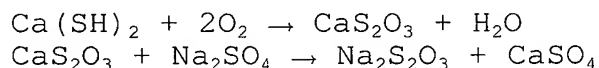
Thus the mid-point of the reaction is signaled by the sudden appearance in the reactor gaseous effluent of hydrogen sulfide at a concentration twice that of the incoming carbon dioxide. The end-point of the reaction is signaled by a break-through of carbon dioxide and the cessation of evolution of hydrogen sulfide gas as the residual dissolved hydrogen sulfide is stripped from the remaining aqueous mother liquor by the flue gas. The precipitate is settled, filtered, washed with water on the filter device, dried, bagged and sold. The evolved hydrogen sulfide gas, diluted with the remains of the flue gas, might be absorbed in an aqueous solution of caustic soda in order to manufacture sodium sulfide or might be sent as feed stock to any one of several types of commercially proven plants for conversion by partial oxidation with air or other means to produce elemental sulfur.



Industrial History of Calcium Sulfide

5 Calcium sulfide has long been recognized as being insoluble  
in water. A process for the manufacture of soda ash from salt  
and sulfuric acid was first established at St. Denis, France, by  
Leblanc in 1792. In the Leblanc process, as it was known, common  
salt was reacted with sulfuric acid to make sodium sulfate  
10 (solid) and hydrochloric acid (gas).

The sodium sulfate was then reacted at high temperature with  
limestone (calcium carbonate) and coal to produce a "black ash"  
comprised of sodium carbonate, calcium sulfide, residual carbon  
15 and coal ash. The sodium carbonate was then leached with water  
from the insoluble calcium sulfide, carbon and coal ash and  
subsequently separated by evaporation in a commercially pure  
form. The Leblanc process was replaced as the leading source of  
soda ash worldwide by the ammonia-soda or Solvay process only  
20 after 1885. The *Encyclopedia of Chemical Technology*, 3rd  
edition, Kirk & Othmer, (22: 118), mentions that calcium  
hydrosulfide,  $\text{Ca}(\text{SH})_2$ , from Leblanc process waste was used to  
manufacture sodium thiosulfate.



Many attempts have been made to devise processes to recover  
sulfur or sulfuric acid from natural gypsum or from the process  
30 waste created by phosphoric acid manufacture or lime/limestone  
flue gas desulfurization (FGD) scrubbing. The Müller-Kühne  
process to convert gypsum to sulfuric acid and cement was  
commercialized by Bayer in Germany in 1916-1918. The heart of

that development is a process which produces a gas stream of sulfur dioxide suitable for manufacture of sulfuric acid and a clinker suitable for the manufacture of Portland cement. The Müller-Kühne process is offered commercially today. A two stage fluidized bed reactor system to reduce gypsum to sulfur dioxide and clinker is disclosed in U.S. Patent No. 4,102,989 to Wheelock, and assigned to Iowa State University. It sometimes is referred to as the ISU process. A major drawback of the Müller-Kühne and ISU processes is that if the FGD waste product contains more than a stoichiometric quantity of unburned carbon from fly ash, the reaction cannot be controlled to produce clinker and sulfur dioxide as desired but instead produces calcium sulfide admixed with the other materials as the only product. Separating excess carbon contained in the fly ash in order to make the process operate as desired would require a very expensive duplication of bag-house equipment in the FGD facility or the expensive import of carbon free calcium sulfate/sulfite material for blending with FGD waste material feed stock.

The thermal reduction of gypsum both experimentally by the United States Bureau of Mines (USBM) and commercially by Elcor Co. is discussed in the *Encyclopedia of Chemical Technology*, 3rd edition, Kirk & Othmer, (22: 91,92). The Bureau of Mines performed extensive research work in the late 1960's on two processes (*Sulfur* 80 1969) for the production of elemental sulfur from gypsum,  $\text{CaSO}_4$ , via reduction roasting with coal or reducing gas at 900-950°C to make calcium sulfide. The first USBM process was to slurry the calcium sulfide in water, to carbonate the slurry with flue gas containing carbon dioxide in order to precipitate calcium carbonate mixed with the gangue and ash and evolve hydrogen sulfide which could then be reduced to elemental sulfur in a Claus process plant. The second USBM process

involved the reaction of sodium chloride (presumably with carbon dioxide, water and calcium sulfide) in a counter-current ion-exchange system to make sodium carbonate, calcium chloride and elemental sulfur. Three tons of each by-product were made for every ton of sulfur in this process. Neither process has ever been commercialized but some of the technology from the first USBM process was employed in a plant built in west Texas by Elcor Co. (*Chem. Engineering News*, **21**, March 20, 1967) and briefly operated commercially in 1968. Elcor used a shaft kiln and reformed natural gas to reduce gypsum to calcium sulfide which was then quenched in water, ground in a ball mill, mixed with more water and contacted with carbon dioxide from the shaft kiln to evolve hydrogen sulfide and precipitate calcium carbonate mixed intimately with sulfide ash impurities. The hydrogen sulfide was reduced to elemental sulfur in a Claus plant. There was no market for the impure calcium carbonate and although most technical problems were said to have been solved, the unprofitable plant was shut down due to prohibitive production costs such as operation of the ball mill.

There remains a need in the art for improved methods of flue gas desulfurization, and processing sulfur-containing materials such as poorly soluble metal sulfides.

#### SUMMARY OF THE INVENTION

In accordance with the present invention, a method is provided for processing sulfur-containing material derived from a source selected from the group consisting of sulfur-containing, carbon-containing fuel and gaseous combustion product of sulfur-containing, carbon-containing fuel. The method comprises providing a calcium sulfide-containing mixture derived from said

source by reacting sulfur-containing material in said source with a calcium-containing material so as to produce said calcium sulfide-containing mixture further containing impurities. The method further comprises leaching a majority of said calcium sulfide from said calcium sulfide-containing mixture in a first aqueous solution containing hydrogen sulfide in an amount sufficient to dissolve said majority of said calcium sulfide in said first aqueous solution, so as to form a second solution containing calcium hydrosulfide. The second solution containing said calcium hydrosulfide is separated from said insoluble impurities, and a calcium-containing material selected from the group consisting of calcium carbonate and calcium hydroxide is precipitated from the second solution.

The invention further includes an apparatus comprising a leaching zone containing a calcium sulfide-containing mixture derived from a source selected from the group consisting of sulfur-containing, carbon-containing fuel and gaseous combustion product of sulfur-containing, carbon-containing fuel, within which leaching zone a majority of the calcium sulfide from said calcium sulfide-containing mixture is leached in a first aqueous solution containing hydrogen sulfide in an amount sufficient to dissolve said majority of said calcium sulfide in said first aqueous solution, so as to form a second solution containing calcium hydrosulfide. The apparatus includes a separation system connected to the leaching zone, through which the second solution containing said calcium hydrosulfide is separated from said insoluble impurities. The apparatus further includes a precipitating zone operatively associated with the separating system, within which a calcium-containing material is precipitated from the second solution, said calcium-containing

material being selected from the group consisting of calcium carbonate and calcium hydroxide.

5 The invention also is directed to a method of processing a metal sulfur compound-containing material, comprising heating a first metal sulfur compound-containing mixture in the presence of a reducing agent, said metal being selected from the group consisting of calcium and strontium, the sulfur compound being selected from the group consisting of sulfates and sulfites, so  
10 as to convert the first metal sulfur compound-containing mixture into a second mixture including impurities and a corresponding metal sulfide of said metal. A majority of said metal sulfide is leached from said second mixture in a first aqueous solution containing hydrogen sulfide in an amount sufficient to dissolve  
15 said majority of said metal sulfide in said first aqueous solution, so as to form a second aqueous solution containing a corresponding metal hydrosulfide of said metal. The second solution containing said metal hydrosulfide is separated from said impurities, and a metal-containing material selected from  
20 the group consisting of a metal carbonate of said metal and a metal hydroxide of said metal is precipitated from said second solution.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

25 The present invention permits utilization of technologies and chemistry to selectively absorb sulfur dioxide from other gases by lime/limestone scrubbing (flue gas desulfurization), to economically transport the intermediate product preferably in a  
30 dry form in order to minimize transportation and drying costs or as a slurry if desired, to roast the dry material with coal or other reducing agents in order to convert it to a mixture of

crude calcium sulfide and impurities, to leach the calcium sulfide in an aqueous solution in order to separate the calcium sulfide from gangue and other impurities, to precipitate calcium in a commercially pure form either as the carbonate by the addition of carbonate ions or as the hydroxide by removing hydrogen sulfide by physical means, and to reduce the hydrogen sulfide removed from the mother liquor to elemental sulfur by partial oxidation. All prior attempts to utilize such an overall process sequence to make elemental sulfur and high purity calcium carbonate from lime/limestone scrubbing effluents have been determined either to be impossible due to the very low solubility of calcium sulfide in water or have proven to be uneconomical due to an inability to separate calcium sulfide from impurities in the system prior to precipitation so as to profitably manufacture marketable calcium carbonate. There has been no prior recognition at all that calcium hydroxide can be made easily from calcium sulfide by hydrolysis and the withdrawal of hydrogen sulfide. The present invention avoids the delicate control and stoichiometry problems involved with prior art combined reduction/oxidation processes, can produce elemental sulfur rather than sulfur dioxide or sulfuric acid which are both much more difficult and expensive to store or transport to market than sulfur, and can separate calcium compounds as more valuable products from other clinker residue components.

Strontium sulfide and Hydrogen Sulfide

Strontium sulfide black ash is made commercially from strontium sulfate ore. The strontium black ash is leached with water to obtain a strontium sulfide solution which is sometimes converted to strontium carbonate by the addition of carbon dioxide in a manner similar to the manufacture of barium carbonate. The yield of barium using the process is about 95%, more or less, but the yield of strontium from its ore by reductive roasting, water leaching and carbonation has been observed to be only perhaps 50% to 75% more or less. Heretofore, there has been a lack of satisfactory explanation for the lower yield.

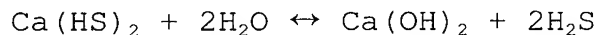
As noted above, calcium sulfide is essentially insoluble in water. It has been commercially demonstrated to be impracticable and generally considered impossible, prior to this invention, to utilize any variation of the commercial barium process technology and chemistry for the purification of calcium sulfide in order to economically manufacture other commercially pure calcium salts.

This invention permits one to integrate into an otherwise unattainable regenerative flue gas scrubbing process, or into a process to economically recover sulfur from gypsum, a means to increase the solubility of calcium sulfide in water from essentially insoluble (0.0121 gm CaS/100 ml solution at 15°C, 0.0212 gm CaS/100 ml solution at 20°C, or 0.4614 gm CaS/100 ml solution at 100°C) to very soluble (19 to over 21 gm CaS/100 ml solution at 20°C) by the addition of varying amounts of hydrogen sulfide, a chemical readily available in the process which is fully recovered and recycled.

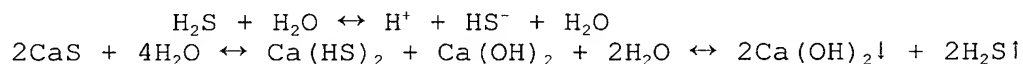
Norbert A. Lange, *Handbook of Chemistry*, (1946) Sixth Edition, p. 182-3, teaches that calcium sulfide decomposes in both cold and hot water. Research by A. Mourlot (1897), *Compt. Rend.*, **127**, p. 408, demonstrated that when crystalline calcium sulfide was heated with air-free water, it rapidly dissociated into calcium hydrosulfide and calcium hydroxide and evolved hydrogen sulfide. The decomposition demonstrates that the hydrosulfide ion calcium bond, unlike the hydrosulfide barium bond in the barium sulfide hydrolysis product, is easily broken in aqueous solution releasing hydrogen sulfide and precipitating insoluble calcium hydroxide. But William F. Linke, *Solubilities, Inorganic and Metal-Organic Compounds*, (1958), Fourth Edition, Vol. I., p. 657-8, American Chemical Society, Washington, DC, refers to work of E.H. Riesenfeld and H. Feld, (1921), *Z. Anorg. Allgem. Chem.*, **116**, p. 213-227, on the solubility of calcium sulfide in air free water and in solutions containing hydrogen sulfide (see Table 2 herein) concluding, "From the result at 20° and 760-mm pressure [ $\text{H}_2\text{S}$ ] it was calculated that 206.5 gms. of  $\text{CaS}$  are present per liter. The corresponding figure for  $\text{CaS}$  in  $\text{H}_2\text{O}$  alone at 20° and 760-mm pressure of air is 0.212 gms per liter. Hence  $\text{H}_2\text{S}$  increases the solubility of  $\text{CaS}$  in water almost 1000 times." The present invention utilizes this to increase the solubility of calcium sulfide in water by three orders of magnitude (almost 1000 fold) by introducing an excess of hydrogen sulfide in one embodiment, to provide a unique integrated process previously considered impossible for the economic recovery of commercially pure calcium and sulfur values from crude impure calcium sulfide. The calcium can be easily precipitated from the clarified aqueous solution of calcium sulfide as calcium carbonate by the addition of carbonate ions, usually in the form of carbon dioxide. The present invention also utilizes the same reversible chemistry to reclaim if desired a commercially pure



grade of calcium hydroxide from the decanted and/or filtered calcium hydrosulfide solution by simply removing hydrogen sulfide from the solution by boiling the solution, vacuum, steam stripping, inert gas stripping, or other appropriate means or a combination thereof. H. von Miller and C. Opl, (1884), *German Pat., D.R.P.*, 28067, state that if a solution of calcium hydrosulfide is evaporated, hydrogen sulfide is expelled and calcium hydroxide is crystallized due to hydrolysis.



Hydrogen sulfide dissolves in the water in proportion to its partial pressure above the water and drives the reversible reaction away from the insoluble calcium hydroxide toward the very soluble calcium hydrosulfide according to the following equations. A withdrawal of hydrogen sulfide from the system reverses the equations to precipitate calcium hydroxide. E.H. Riesenfeld and H. Feld, (1921), *op. cit.*, report that a decrease in partial pressure of air-free hydrogen sulfide in contact with a solution of calcium hydrosulfide can result in the crystallization of purified calcium sulfide rather than calcium hydroxide.



The process invention, which permits these achievements, also is applicable to improving the currently practiced process to manufacture strontium sulfide from strontium sulfate ore by high temperature reduction, followed by water leaching and carbonation, in order to make strontium carbonate. This invention greatly improves the economics of strontium carbonate production by very significantly increasing the recovery or yield of strontium and permits the alternative production of strontium hydroxide if desired.

The similarities and unique differences of calcium, strontium and barium and their compounds are described, including many references to basic research, by J.W. Melor in A *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, volume III, pages 619-908, (1923), Longmans, Green and Co., London. Barium sulfate, strontium sulfate and calcium sulfate, and mixtures thereof, each have been commercially roasted with coal and other reducing agents to produce "black ash" wherein their respective sulfates have been converted to sulfides. It should be noted that calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , is only slightly soluble in water, decreasing from 0.185% by wt. at 0°C to 0.077% by wt. at 100°C while barium hydroxide is very soluble in water, increasing from 1.64% by wt. at 0°C to over 50% by wt. at 80°C according to Lange's Handbook of Chemistry, Sixth Edition, 1946, p. 1224-1225. By comparison, strontium hydroxide,  $\text{Sr}(\text{OH})_2$ , is moderately soluble in water as shown in Table 5 herein, increasing from 0.03% wt. at 0°C to 15.90% wt. at 100°C. The hydrosulfides of calcium, barium and strontium are very soluble as shown respectively in Tables 2, 4 and 6 herein.

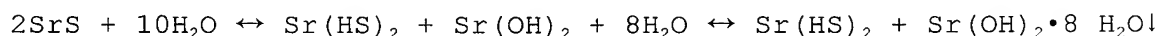
Melor describes the sulfides in particular in Section 13. Calcium, Strontium, and Barium Sulphides, pages 740-758. He states that A. Mourlot (1897), *Compt. Rend.*, **127**, p.408, demonstrated that when crystalline calcium sulfide was heated with air-free water, it rapidly dissociated into calcium hydrosulfide and calcium hydroxide and evolved hydrogen sulfide. E. Terres and K. Bruckner, (1920), *Zeit. Elektrochem.*, **26**, 25, found that strontium sulfide heated with air free water reacted in a manner similar to calcium sulfide evolving hydrogen sulfide. Terres and Bruckner reported strontium hydroxide crystals are deposited on cooling a solution of strontium sulfide dissolved in boiling water but they found that when barium sulfide is

extracted with water at all temperatures up to boiling, only barium hydroxyhydrosulfide,  $\text{Ba}(\text{SH})(\text{OH}) \cdot 5\text{H}_2\text{O}$ , was formed. This they found to be stable and under no conditions were they able to separate barium hydroxide by crystallization from the barium sulfide solution.

These differences in the chemistry of barium, strontium and calcium, known for up to a century or more but heretofore not recognized for their profound significance, are fundamental to the present invention for the separation of calcium and sulfur values from impurities associated with sulfur compounds of calcium and for an improved recovery yield of strontium compounds from sulfate ore as well as essentially complete recovery of the sulfur from sulfur compounds of strontium.

The present invention now explains why the barium process is not well suited for use in recovering strontium and identifies the changes needed to obtain higher yields of strontium at lower overall costs.

When strontium sulfide dissolves in water it hydrolyzes and dissociates into equal molecular portions of slightly soluble (3.5% by weight in water) strontium hydroxide and very soluble (33.2% by weight in water) strontium hydrosulfide. As the concentration of strontium sulfide in solution increases the solubility product constant of strontium hydroxide is exceeded and it crystallizes out of solution as the octohydrate. (see Table 6 herein)



E. Terres and K. Bruckner, (1920), *Zeit. Elektrochem.*, 26, 25, found that strontium sulfide heated with air free water

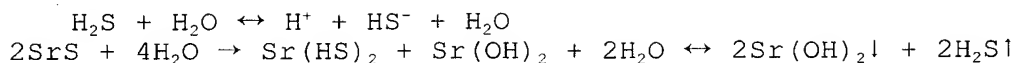
reacted in a manner similar to calcium sulfide evolving hydrogen sulfide. C.L. Berthollet, (1802), *Journ. Polyt.*, 4, 315, reported strontium hydroxide octohydrate crystals were formed when a boiling solution of strontium sulfide was cooled. H. Rose, (1842), *Pogg Ann.*, 55, 415, 533, reported the cooled mother liquor contained strontium hydrosulfide and found that if strontium sulfide is treated with a small proportion of water, strontium hydrosulfide passes into solution first, then if the residue is again treated with water, strontium hydroxide is mainly dissolved. The latter confirms the law of mass action with the more soluble strontium hydrosulfide preferentially dissolved while the former demonstrates that the strontium to hydrosulfide ion bond is broken in aqueous solution less readily than the calcium to hydrosulfide bond but the solution still can release hydrogen sulfide with some of the strontium hydrosulfide converted to the much less soluble hydroxide. The hydrosulfide to barium bond, unlike its bond to both calcium and strontium, is tenacious. Barium sulfide dissolved in water yields only barium hydroxyhydrosulfide pentahydrate crystals,  $\text{Ba}(\text{SH})(\text{OH}) \cdot 5\text{H}_2\text{O}$ , upon cooling with no barium hydroxide crystals formed unless an excess of hydroxide is added.

Terres and Bruckner (1929) prepared solubility tables for the system  $\text{Sr}(\text{OH})_2\text{-Sr}(\text{SH})_2\text{-H}_2\text{O}$  which are reproduced in W.F. Linke, op cit., p.1515 (reproduced as Table 6 herein). These tables demonstrate that the solubility of strontium hydroxide in water at all temperatures decreases with increasing concentrations of strontium hydrosulfide as predicted by the law of mass action. For example, at 60°C, the solubility of strontium hydroxide in water alone is about 3.25% to 3.6% by weight, the solubility of strontium hydrosulfide in water alone is about 33.2% by weight, but the solubility of strontium hydroxide decreases to 1.75% by

weight in the presence of 25% by weight of strontium hydrosulfide and further decreases to zero in a solution saturated with strontium hydrosulfide. It is obvious with these facts in mind that the water leaching of a strontium sulfide black ash with water alone will result principally in a solution of strontium hydrosulfide while a considerable quantity of strontium hydroxide will report to the insoluble black ash residue thus resulting in a yield of as little as about half of the strontium contained in the black ash.

The present invention greatly increases the recovery or yield of strontium by avoiding the loss as insoluble hydroxide in the leaching operation through the addition of hydrogen sulfide to the leaching solution. The present invention also utilizes the reversible chemistry to reclaim if desired a portion of the strontium contained in the decanted and/or filtered strontium hydrosulfide solution as a commercially pure grade of strontium hydroxide by simply removing hydrogen sulfide from the solution by heating and cooling, vacuum, steam stripping, inert gas stripping, or other appropriate means or a combination thereof. Care must be taken to avoid the oxidation of strontium sulfide at higher temperatures to strontium sulfate by water vapor as reported by O. Schumann, (1877), *Liebig's Ann.*, **187**, p. 286.

Hydrogen sulfide dissolves in water in proportion to its partial pressure above the water according to Henry's law and drives the reversible reaction to convert slightly soluble strontium hydroxide,  $\text{Sr}(\text{OH})_2$ , to very water soluble strontium hydrosulfide,  $\text{Sr}(\text{HS})_2$ , according to the following equations. A withdrawal of hydrogen sulfide from the system can reverse the equations to precipitate strontium hydroxide.



It is possible to decant both calcium and strontium hydrosulfide aqueous solutions from insoluble impurities in a manner similar to the commercial decanting of barium hydroxyhydrosulfide liquor from its similar impurities. The required concentration of dissolved hydrogen sulfide and hence hydrosulfide ions is less than that which is in equilibrium with one atmosphere partial pressure of hydrogen sulfide in contact with the water as illustrated in Tables 2 and 6 herein. Impurities usually include gangue from the ore, ash and unburned carbon from the coal or other reducing agent and metal sulfides such as iron. All of these impurities are insoluble in both water and water containing hydrosulfide ions. The decanted solution can be filtered if desired to remove any remaining entrained solids.

#### Tables of Solubilities

##### Calcium Sulfide CaS

Compiled verbatim from: Linke, William F., *Solubilities, Inorganic and Metal Organic Compounds, A-Ir, A Compilation of Solubility Data from the Periodical Literature, Volume I, Fourth Edition, A Revision and Continuation of the Compilation Originated by Atherton Seidell, 1958, American Chemical Society, Washington, D.C., p. 657-658.*

Table 1

Solubility of Calcium Sulfide in Water in the Absence of Air  
(Foerster and Kubel, 1924)

The sample was prepared by heating calcium sulfite for 1 hour at 700-750°C. It contained 12.1% CaS.

	t°C	Minutes Digested with H <sub>2</sub> O	Gms. Sample digested per 100 gms. H <sub>2</sub> O	Gms. CaS dissolved per 100 cc sat. soln.	Per cent of the used CaS dissolved
10	15	15	2.5414	0.0090	2.9
	15	15	2.3759	0.0100	3.5
15	15	60	2.4707	0.0121	4.0
	100	15	3.2079	0.1450	37.4
20	100	60	5.3080	0.4614	71.8

Table 2

Solubility of Calcium Sulfide in Water and in Aqueous Solutions  
of Hydrogen Sulfide  
at 20°C  
(Riesenfeld and Feld, 1921)

The sample of calcium sulfide contained CaSO<sub>4</sub>, CaO, and C. Water saturated with the sample at 20° contained 0.2120 gms. CaS, 0.3881 gms. CaSO<sub>4</sub> and 0.1786 gms. CaO per liter. For the solubility in the presence of H<sub>2</sub>S an apparatus constructed entirely of glass was used. The air was completely displaced with H<sub>2</sub>S to insure that only this gas was present. The equilibrium was approached from below and from above by changing the pressure of the H<sub>2</sub>S. The influence of time upon the

attainment of equilibrium was found to be considerable, but the rate was shown to be a reaction of the first order and from it the final equilibrium could be estimated. The manometer was read in the beginning and after the solution had been shaken and from this it was known whether equilibrium was being approached from above or below. The results of the analyses in grams of S per 100 cc. Were plotted and from the curves and the calculations from Henry's law on the proportion of the S in the form of  $H_2S$ , the difference gave that present as calcium sulphhydrate and calcium sulfide.

	Pressure of $H_2S$ in mm. Hg	Gms. $Ca(HS)_2$ per 100 cc. Sat. soln. at			Pressure of $H_2S$ in mm. Hg	Gms. $Ca(HS)_2$ per 100 cc. Sat. soln. at		
		0°	20°	40°		0°	20°	40°
15	100	26.61	24.87	21.97	500	31.17	28.76	26.61
	150	28.76	25.78	23.47	550	31.42	29.09	27.02
	200	29.45	26.19	24.24	600	31.66	29.43	27.35
	250	29.92	26.86	24.79	650	31.83	29.65	27.69
	300	30.09	27.45	25.20	700	32.08	30.09	28.04
20	350	30.43	27.69	25.50	750	32.33	30.34	28.35
	400	30.67	28.10	25.94	760	32.41	30.42	28.44
	450	30.92	28.31	26.25				

From the result at 20° and 760 mm. pressure it was calculated that 206.5 gms. of  $CaS$  are present per liter. The corresponding figure for  $CaS$  alone at 20° and 760 mm. pressure of air is 0.212 gm per liter. Hence  $H_2S$  increases the solubility of  $CaS$  in water almost 1000 times.

### Barium Sulfide $BaS$

Compiled verbatim from: Linke, William F., *Solubilities, Inorganic and Metal Organic Compounds, A-Ir, A Compilation of Solubility Data from the Periodical Literature, Volume I, Fourth Edition, A Revision and Continuation of the Compilation Originated by Atherton Seidell, 1958, American Chemical Society, Washington, D.C., p.386-387.*



Table 3  
Solubility of Commercial Barium Sulfide in Water  
(Terres and Bruckner, 1920)

The sample of barium sulfide contained 87.2% BaS, 4.33% Ba(OH)<sub>2</sub> and 8.47% Fe and Mn oxides. Due to the oxidizing action of air upon the sulfhydrate the solubility determinations were conducted in an atmosphere of hydrogen. The mixtures were constantly agitated for many hours.

t°	Gms. per 100 gms. <u>sat. soln.</u>		Corresponding BaS in solution
	Ba(OH) <sub>2</sub>	Ba(SH) <sub>2</sub>	
0	2.05	2.42	4.03
20	3.28	3.90	6.48
40	5.32	6.32	10.5
60	8.14	9.68	16.5
80	10.62	12.61	21.0
100	12.80	15.25	25.25

Table 4  
Solubility of Barium Hydrogen Sulfide in Water  
(Terres and Bruckner, 1920)

t°	Gms. Ba(SH) <sub>2</sub> per 100 gms. sat. soln.
-15	32.0
0	32.6
20	32.8
40	34.5
60	36.2
80	39.0
100	43.7

**Strontium Sulfide SrS**

Compiled verbatim from: Linke, William F., *Solubilities, Inorganic and Metal Organic Compounds, K-Z, A Compilation of Solubility Data from the Periodical Literature, Volume II, Fourth Edition, A Revision and Continuation of the Compilation Originated by Atherton Seidell, 1965, American Chemical Society, Washington, D.C., p.1514-1515.*

Table 5  
Solubility of Strontium Hydroxide in Water  
(Scheibler, 1883)

t°	<u>Grams per 100 grams solution</u>	
	SrO	Sr(OH) <sub>2</sub> •8H <sub>2</sub> O
0	0.35	0.90
10	0.48	1.23
20	0.68	1.74
30	1.00	2.57
40	1.48	3.80
50	2.13	5.46
60	3.03	7.77
70	4.35	11.16
80	6.56	16.83
90	12.0	30.78
100	18.6	47.71

Later determinations agreeing closely with Scheibler, 1883, were given by Grube and Hussbaum, 1928, and Ahrens, 1930.

Table 6  
The System  $\text{Sr}(\text{OH})_2 - \text{Sr}(\text{SH})_2 - \text{H}_2\text{O}$   
(Terres and Bruckner, 1929)

These results when plotted give curves composed of two  
5 branches corresponding respectively to the solid phases  
 $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Sr}(\text{SH})_2 \cdot 4\text{H}_2\text{O}$ .

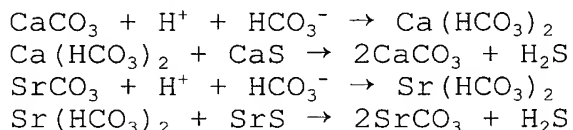
<u>Grams per 100 grams saturated solution</u>							
	$\text{Sr}(\text{OH})_2$	$\text{Sr}(\text{SH})_2$	$\text{Sr}(\text{OH})_2$	$\text{Sr}(\text{SH})_2$	$\text{Sr}(\text{OH})_2$	$\text{Sr}(\text{SH})_2$	$\text{Sr}(\text{OH})_2$ $\text{Sr}(\text{SH})_2$
10	<u>Results at 0°</u>		<u>Results at 20°</u>		<u>Results at 40°</u>		<u>Results at 60°</u>
	0.41	0.00	0.82	0.00	1.75	0.00	3.63 0.00
	0.30	1.56	0.72	5.9	1.65	1.40	3.15 1.60
	0.25	6.68	0.70	11.4	1.60	4.87	3.04 6.08
	0.22	12.65	0.62	15.8	1.60	10.83	3.16 11.85
15	0.20	14.80	0.60	18.3	1.55	15.93	3.15 16.72
	0.16	18.20	0.55	20.3	1.50	20.00	1.75 25.0
	0.15	19.05	1.00[sic]	24.0	1.10	24.10	1.75 26.6
	0.10	23.40	0.25	26.0	0.80	26.20	0.60 30.8
	0.10	24.80	0.20	26.8	0.42	28.30	0.10 33.6
20	0.20[sic]	27.5	0.15	27.5	0.30	29.25	0.00 33.2
	0.00	27.50	0.00	29.7	0.10	31.60	0.00 31.60

<u>Grams per 100 grams saturated solution</u>			
	$\text{Sr}(\text{OH})_2$	$\text{Sr}(\text{SH})_2$	$\text{Sr}(\text{OH})_2$ $\text{Sr}(\text{SH})_2$
25	<u>Results at 80°</u>		<u>Results at 100°</u>
	7.78	0.00	23.20 0.00
	5.60	5.60	14.00 7.40
	5.00	9.50	0.15 37.80
30	4.88	15.50	0.00 37.80
	4.10	19.60	
	2.70	27.50	
	2.10	28.00	
	1.40	30.40	
35	0.05	35.60	
	0.00	35.60	

Certain simple but important differences in process  
40 chemistry must be understood when changing from the carbonation  
of a barium sulfide aqueous solution (in reality an equimolar  
solution of barium hydroxide and barium hydrosulfide) in contact

with air to the carbonation of a calcium or strontium hydrosulfide aqueous solution maintained under an atmosphere of hydrogen sulfide preferably free of oxygen.

5           Barium carbonate is not soluble in carbonic acid, an aqueous solution of carbon dioxide, hence the end-point of the of the carbon dioxide absorption for barium carbonate precipitation is not critical and is routinely overshoot. Calcium or strontium carbonates will dissolve to a limited extent in water containing  
10 an excess of carbon dioxide to form the slightly more soluble calcium or strontium bicarbonates. The recycling of calcium or strontium bicarbonates in mother liquor would result in a decreased production of the desired calcium or strontium carbonate product due to the loss of precipitated calcium or  
15 strontium as their carbonates reporting to the gangue and impurities waste stream if a mother liquor containing the respective bicarbonate were to be recycled without further treatment before being used to dissolve another batch of crude calcium or strontium sulfide.



25           Control of the addition of carbon dioxide to a rather precise endpoint in the conversion of calcium hydrosulfide to calcium carbonate is therefore necessary if one is to prevent these undesired process yield losses.

30           A small amount of calcium carbonate in the presence of water saturated with hydrogen sulfide gas will be hydrolyzed reversibly to form calcium hydrosulfide and calcium bicarbonate. It therefore is desirable to strip the remaining hydrogen sulfide gas from the mother liquor after carbonation in order to complete

the precipitation of the calcium as the carbonate before recycling the mother liquor to dissolve another batch of calcium sulfide. This could be done after the primary decantation and washing of the main precipitated calcium carbonate product stream. It is probable but not yet proven that the same chemistry applies to strontium carbonate. The stripping gas should contain no excess carbon dioxide in order to avoid dissolving the residual solid calcium carbonate as the bicarbonate. It is preferable that the stripping gas contain no free oxygen which could oxidize some of the hydrogen sulfide to sulfur which then would co-precipitate with and contaminate the precipitated residual calcium carbonate.

The carbonation of barium sulfide aqueous solution is often accomplished with flue gas containing perhaps 10% to 12% more or less by volume of carbon dioxide and perhaps 3% more or less by volume of oxygen. It is well known to those skilled in the art that this small concentration of oxygen is sufficient to oxidize a portion of the sulfide compounds present to polysulfides or other sulfur compounds which report as trace amounts of sulfur contamination in the precipitated barium carbonate. E. H. Riesenfeld and H. Feld, *Zeit. Anorg. Chem.*, 116, 213, 1921, prepared purified calcium monosulfide, CaS, by first dissolving the sulfide in an aqueous solution of hydrogen sulfide, then removing the hydrogen sulfide from the solution of calcium hydrosulfide by suction. They noted that if air be not excluded, the solution of hydrosulfide will be yellow owing to the formation of polysulfides, etc. They concluded that all operations therefore should be conducted in an atmosphere of hydrogen sulfide. E. Becquerel, *Ann. Chim. Phys.*, (3), 22, 244, 1848, earlier emphasized his observation that if air be not

excluded the sulfide would be partially oxidized to sulfate. This chemistry also applies to strontium sulfide solutions.

These observations of process chemistry lead to several factors which indicate that it is both economically and technically preferable to install a simple absorber-stripper unit to recover carbon dioxide from the source flue gas step for carbonation of calcium or strontium hydrosulfide rather than to use flue gas directly.

Carbonation of a calcium or strontium hydrosulfide solution with flue gas containing about 11%  $\text{CO}_2$  and 3%  $\text{O}_2$  would produce an off gas consisting of perhaps 20% more or less by volume hydrogen sulfide and 2.7% more or less oxygen. This off-gas would be recycled to dissolve the next sequential batch of black ash. A lowered partial pressure of hydrogen sulfide in equilibrium with the water solute used to dissolve calcium or strontium sulfide will appreciably reduce the solubility of calcium or strontium sulfide in the solution as shown in Tables 2 and 6 herein. This would require a larger volume of solution and larger equipment to maintain a given production rate than with a higher assay hydrogen sulfide gas.

The presence of even 2.7% oxygen in contact with the mother liquor during the solution of calcium or strontium sulfide from black ash would form soluble polysulfides. Those would decompose and precipitate sulfur or compounds thereof when the sulfide ions are depleted during carbonation and would contaminate the precipitated otherwise high quality calcium or strontium carbonate.

Carbonation with flue gas which contains oxygen will form polysulfides during the carbonation process which would contaminate the product calcium or strontium carbonate with sulfur when they decompose upon the depletion of sulfide ions.

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An initial stream of 20% hydrogen sulfide which is subsequently and substantially depleted by partial absorption could present an environmental disposal problem. At the very least, if such a dilute stream of hydrogen sulfide were to be recycled to the primary equipment fire box it would increase the quantity of sulfur dioxide which would have to be scrubbed from the flue gas leaving that firebox. A stream of high purity hydrogen sulfide could be recycled to extinction within the black ash dissolving system with a simple blower thus requiring very little recycle to the primary firebox.

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The recovery of elemental sulfur from hydrogen sulfide is most economically performed in a Claus process plant by partial oxidation using air. A smaller and less expensive Claus plant can be used at an appreciably lower operating cost to recover a given quantity of sulfur from a gas containing say 98% hydrogen sulfide than from a gas containing only 20% hydrogen sulfide.

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A simple absorber-stripper unit can absorb carbon dioxide from the flue gas and deliver it at a concentration of 95% or preferably more carbon dioxide, zero oxygen and balance nitrogen to the calcium or strontium hydrosulfide carbonation process. A calcium or strontium hydrosulfide carbonation step fed with 95% carbon dioxide gas would produce about a 97.5% concentration of hydrogen sulfide. This high concentration of hydrogen sulfide would be very suitable to be contacted directly with recycled mother liquor in order to dissolve the next batch of calcium or

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strontium sulfide and it would serve as an appropriate and economical feed stock for the Claus sulfur recovery plant. A feed stock stream of high strength carbon dioxide could be mixed with a stream of hydrogen sulfide gas recycled through the carbonator if desired in order to control the reaction parameters and particle size distribution of the precipitated calcium or strontium carbonate.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figs. 1 and 2A-2F are schematic diagrams showing embodiments of an apparatus for carrying out the present invention.

One embodiment of the present invention can be carried out in an apparatus as shown in the accompanying figures.

Fig. 1 shows a boiler 10 from which sulfur dioxide-containing gaseous emissions pass through line 12 into spray absorber 14.

A raw lime supply 16 supplies a lime bin 18 through line 20. Lime is fed from lime bin 18 into lime slaker 22. Water from source 24 passes through line 26 into lime slaker 22, to be mixed with the lime to form lime milk. Lime milk flows from lime slaker 22 into lime milk tank 28 through conduit 30. Lime milk then passes through regulator 32 and line 34 and through control valve 36 to be injected into spray absorber 14 as droplet spray 38.

It is within spray absorber 14 (the absorption zone) that sulfur dioxide from the gaseous emission entering through line 12 is absorbed into the calcium-containing absorbent such as the



droplet spray 38 of lime milk. Control valve 36 controlling the amount of lime milk injected into spray absorber 14 is controlled by SO<sub>2</sub> control 66 which controls lime milk dosing to meet local emissions requirements.

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Excess lime dust from spray absorber 14 is collected in dust collector 42 through line 44, also under control of the flue gas outlet temperature control 40, as is known in the art.

10       Recycle dust from dust collector 42 is passed through lines 44a and 44b, to line 46, and then into recycle material bin 48. Recycle material passes from bin 48 into mix tank 50, where it is mixed with water from water source 52, entering mix tank 50 through line 54. Recycle lime mixed with water flows through  
15       conduit 56 into recycle feed tank 58. Recycle lime milk then can pass from recycle feed tank 58 through pump 60, line 62 and control valve 64 to be injected into the spray absorber as a portion of droplet spray 38. Control valve 64 is controlled by control 40 which controls recycle slurry dosing to control flue  
20       gas outlet temperature as is known in the art.

Cleaned emissions passing through dust collector 42 are propelled by fan 68 through line 70 into stack 72 to be emitted into the environment.

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The first mixture resulting from the sulfur dioxide being absorbed in the lime within spray absorber 14 passes through line 74 and line 76 either to end product 78 for utilization or disposal, or in accordance with one embodiment of the present  
30       invention through line 80 to storage tank 82 shown in Fig. 2A.

The first mixture from the flue gas desulfurization process stored in storage bin 82 typically contains fly ash, calcium sulfite, calcium sulfate and calcium carbonate.

5           The first mixture from storage bin 82 is fed through line 84, feeder 86 and line 88 into calciner 90, which is a reduction kiln or reactor. A reducing agent such as coal also is fed into the calciner 90 through line 92, if needed, and air is added through line 94. The first mixture is heated in calciner 90, in  
10 the presence of carbon-containing material such as coal, so as to convert the first mixture into a second mixture including primarily calcium sulfide and impurities such as fly ash and the like. The second mixture typically is called black ash in the art, and exits calciner 90 through line 96 and feeder 98 into  
15 leach tank 100.

Dust exits calciner 90 through line 91 to a dust collector 93, which can be a cyclone or bag house type as is known in the art. Exhaust gas from dust collector 93 can be directed to the  
20 stack through line 95, and dust from collector 93 is directed into storage bin 82 through line 97.

Various processing campaigns can be carried out in a single leach tank 100. While three separate leach tanks 100(A), 100(B),  
25 and 100(C), are shown in Figs. 2A and 2B, all actually represent a single leach tank in a battery of such leach tanks in which a dissolving campaign (A) is carried out, sequentially followed by a pump-out campaign (B), and a solution fill campaign (C), which again is followed by a dissolving campaign (A) and so forth  
30 sequentially.

Fig. 2A shows leach tank 100 in the dissolving campaign (A). The first aqueous solution present in tank 100 from fill campaign (C) is saturated with hydrogen sulfide pumped into leach tank 100(A) through line 102 by hydrogen sulfide recycle compressor 104. The hydrogen sulfide continuously added to the first aqueous solution is in an amount sufficient to dissolve the majority of the calcium sulfide continuously added through line 96 and feeder 98 into the first aqueous solution so as to form a second solution containing calcium hydrosulfide. Leaching is facilitated during the dissolving campaign (A) by agitator 106. Hydrogen sulfide can be derived from several sources, including hydrogen sulfide make-up feed line 108 and hydrogen sulfide blanket gas header line 110. Bleed off of inert gas which may build up in the recycled hydrogen sulfide gas is through line 112 to the boiler fire box as necessary.

Fig. 2B shows leach tank 100 in the pump-out campaign (B) and the solution fill campaign (C).

Following the dissolving campaign (A) in leach tank 100 shown in Fig. 2A, the pump-out campaign (B) takes place from leach tank 100 as shown in Fig. 2B. During the pump-out campaign (B), a slurry containing calcium hydrosulfide in solution and impurities is pumped from leach tank 100 through line 114 by slurry pump 116 and through line 118 into settling and decant vessel 120 during a fill and displacement campaign (D). During the pump-out campaign (B) the hydrogen sulfide blanket gas is maintained within leach tank 100 through line 111.

After all of the slurry is pumped from leach tank 100 into settling and decant vessel 120 during the pump-out campaign (B) leach tank 100 is filled with recycle liquor solution through

line 122 in preparation for receiving black ash from calciner 90 in a later dissolving campaign, all the while under a blanket of hydrogen sulfide gas through line 110.

5           Referring back to the settling and decant vessel 120 during fill and displacement campaign (D) shown in Fig. 2B, the sludge settles to or below a level 124, whereas calcium hydrosulfide-containing clear solution 125 passes over weir 126 and exits vessel 120 through overflow weir take-off line 128. This is the  
10           hydrosulfide liquor to be processed downstream in accordance with the present invention.

          However, prior to describing processing of the hydrosulfide liquor downstream in accordance with the present invention, the  
15           backwash campaign (E) and the residual sludge pump-out campaign (F) of the settling and decant vessel 120 will be discussed.

          As with leach tank 100, settling and decant vessel 120 is shown in Figs. 2B and 2C as three separate vessels 120(D), 120(E)  
20           and 120(F), which in fact represent a single settling and decant vessel 120 in a battery of such settling and decant vessels, within which takes place three separate processing campaigns, namely, a fill and displacement campaign (D) shown in Fig. 2B, a backwash campaign (E) also shown in Fig. 2B, and a residual pump-  
25           out campaign (F) shown in Fig. 2C.

          During the backwash campaign (E), wash water is forced through line 130 into settling and decant vessel 120. The wash water is forced through the sludge and over take-off weir 126  
30           through overflow weir take-off line 132. Initially, full strength liquor is directed through line 134 to line 128, but after dilution of the liquor, it is diverted through line 136 to

line 122 and fed to leach tank 100 for the solution fill campaign (C) shown in Fig. 2B, all the while under a blanket of hydrogen sulfide gas.

5            Fig. 2C shows the settling and decant vessel 120 during residue sludge pump-out campaign (F). During this campaign, all of the residue sludge is pumped out of settling and decant vessel 120 through line 138 and residue sludge pump 140 into an optional froth flotation concentrator 142. Froth containing metal  
10           sulfides concentrate can be removed through line 144 and sludge is directed through line 146 to a sludge dewatering filter or centrifuge 148. Dewatered sludge is directed through line 150 to waste disposal or is sintered for use as aggregate, while recycle water is directed through line 152 to line 130 to be used in the  
15           backwash campaign (E) in settling and decant vessel 120.

            Hydrosulfide liquor containing calcium hydrosulfide solution exiting vessel 120 through overflow weir take-off line 128 is pumped by hydrosulfide liquor pump 154 through line 156 into  
20           carbonation reactor 160 during a carbonation reactor fill campaign (G).

            While Figs. 2D and 2E show four separate carbonation reactors 160, these actually represent a single carbonation  
25           reactor from a battery of such reactors during a series of campaigns which are sequentially carried out, including the fill campaign (G), the CO<sub>2</sub> scavenge campaign (H), a carbonation campaign (I), and a pump-out campaign (J).

30           Following filling of carbonation reactor 160 with hydrosulfide liquor during fill campaign (G), a carbonation campaign (I) is carried out.

During the carbonation campaign (I) in carbonation reactor 160, carbon dioxide is introduced through line 162 and recycled through lines 204 and 164, manifold 166 and CO<sub>2</sub> dispersers 168 into carbonation reactor 160 (I).

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The carbon dioxide which is introduced through line 162 comes from a flue gas absorber/stripper unit 170 shown in Fig. 1. The flue gas absorber/stripper 170 receives flue gas through line 172, and can also receive carbon dioxide from an optional calcium carbonate calciner (discussed below) through line 174. Gas containing carbon dioxide enters a carbon dioxide absorber 176 through line 172. Absorbent liquid passing through carbon dioxide absorber 176 passes through line 178 to carbon dioxide stripper 180. Concentrated carbon dioxide gas leaves stripper 180 through line 182, passes through cooler 184 and liquid condensate separator 186, to line 162. Condensate recycles to carbon dioxide stripper 180 through line 188. Cooler 190 reduces the temperature of stripped absorbent liquid returned to absorber 176. Reboiler 192 heated with steam received through line 194 boils the bottoms absorbent liquid from the stripper to furnish absorbent vapor which strips out carbon dioxide from the liquid flowing downward through stripper 180. Gas, from which some carbon dioxide has been removed, passes through line 196 and out stack 172 to atmosphere.

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During the carbonation campaign (I), recycle mixture of carbon dioxide and hydrogen sulfide gases is drawn from carbonation reactor 160 (I) through line 200 by carbonation recycle blower 202 and is introduced into line 164 through line 204.

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A carbon dioxide scavenge campaign (H) takes place in carbonation reactor 160 (H) where residual carbon dioxide is removed from hydrogen sulfide gas which then passes through line 206 to hydrogen sulfide blower 208. Hydrogen sulfide gas passes through line 210, and any excess is directed as an intermediate hydrogen sulfide product through line 212 to a known Claus sulfur recovery unit (not shown). Hydrogen sulfide gas needed by the process system passes through line 214 to line 108 to be used in leach tank 100 (A) during the dissolving campaign (A). After serving in scavenge campaign (H) carbonation reactor 160 is advanced to service in the next carbonation campaign (I).

During the scavenge campaign (H) and carbonation campaign (I) within carbonation reactor 160, calcium carbonate is precipitated from the calcium hydrosulfide-containing solution by carbonation with substantially oxygen-free carbon dioxide gas. The precipitated calcium carbonate is removed from carbonation reactor 160 during a pump-out campaign (J), after substantially complete carbonation, through line 216, as a carbonate slurry by carbonate slurry pump 218.

The carbonate slurry is passed through line 220 to a sectionalized vacuum filter 222, which can be a rotary-type as shown, or any other type as known in the art.

As shown in Fig. 2E, washwater from line 226 exits manifold 228 to be sprayed through nozzles 224 onto the rotary-type sectionalized vacuum filter 222 for washing of the carbonate slurry.

Mother liquor-containing liquid passes from filter 222 through line 230 to a mother liquor filtrate receiver 232.

Separated mother liquor passes through line 234 and mother liquor recycle pump 236 to line 122. Gases drawn from filter 222 pass from the mother liquor filtrate receiver 232 through lines 238, 240 and 242, through two stage vacuum eductors 244 and 246, by steam inputted respectively through lines 248 and 250. The atmosphere pressure exhaust from eductor 246 exits through line 252 to atmosphere, or to line 112 to the boiler fire box if desired.

Washwater containing some mother liquor exits filter 222 through line 254 and passes to washwater receiver 256. Recycle washwater passes from washwater receiver 256, through line 258, then through washwater recycle pump 260 to line 130. Gas from washwater 256 passes through line 262 to line 242 and into vacuum eductors 244 and 246.

Calcium carbonate filter cake is removed from filter 222 at doctor blade 264, and passes along chute 266 to calcium carbonate drier 268 which preferably is an indirect steam-heated type calcium carbonate drier as shown. In the indirect steam-heated type calcium carbonate drier 268 shown, steam enters drier 268 through line 270, and steam condensate exits drier 268 through line 272, providing heat to dry the calcium carbonate. Vapors exit line 274, pass through cooling unit 276 which separates non-condensed gas exhaust passed through line 278, and condensate which passes through line 280 and is returned to the washwater receiver 256.

Dried calcium carbonate passes out of calcium carbonate drier 268 by line 282 and can be sent directly to product bagging 284, or optionally sent to a calciner 286 through conveyor 288. Fuel enters calciner 286 through line 290, and the calcium



carbonate is heated and converted to raw lime and carbon dioxide. Raw lime exits calciner 286 through line 292, and if desired, can be sent to raw lime supply 16 shown in Fig. 1. Carbon dioxide exits calciner 286 through line 174 and can be sent to the carbon dioxide absorber/stripper unit 170 shown in Fig. 1.

Since many modifications, variations and changes in detail may be made to the described embodiments, it is intended that all matter in the foregoing description and shown in the accompanying drawings be interpreted as illustrative and not in a limiting sense.